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# Synthetic Organic Chemicals

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## Organic Chemicals as Analytical Reagents

THE use of organic chemicals for the identification, estimation, or quantitative determination of metals has attracted great interest in recent years. The convenience, speed, and accuracy of analyses employing such compounds have resulted in their wide and ever-increasing acceptance. The principle of such procedures depends upon a specific reaction between the reagent used and the compound to be tested.

Organic reagents may be roughly classified into two groups: the gravimetric, those that react with the unknown to form a complex insoluble in the reaction medium; and the colorimetric, those that produce a color with the metal. For quantitative work, this color must be proportional to the concentration of the unknown. Each group has its advantages, and in many cases, a metal can be determined by whichever type of reaction is more convenient. It can be stated generally that the colorimetric methods are more useful when extremely small amounts such as traces of the metal are to be determined or detected, while the gravimetric methods are more convenient when larger quantities are present.

The ideal reagent is one which is strictly specific in its action; that is, under all conditions it will react with but one material. This condition is rarely obtained, but it has been found not to be so essential as originally considered. Many of the better known reagents react with a great number of metals, but by careful control of various conditions, principally acidity, concentration, and presence or absence of inhibiting salts, the scope is restricted so that they become in effect, specific. In this way, one reagent may be made specific for the determination of more than one metal, and it is even possible to carry out a complete analysis on a material such as an alloy containing many different metals, by the use of a single reagent.

### *Gravimetric Reagents*

It is interesting to observe that the first recorded use of an organic chemical as an analytical reagent dealt with what is still known as the most specific and the closest approach of all such compounds to the ideal. In 1905, Tschugaev reported the use of dimethylglyoxime as a test for nickel, the method being later adapted to give quantitative results. This compound is accepted even today as the best for nickel determinations.

In gravimetric analyses, the metal complexes formed are generally of very low solubility in the reaction medium and of high molecular weight, thus allowing the use of small quantities, yet yielding precipitates of high weight. The crystalline form in which these

complexes are usually obtained permits easy filtration as well as rapid drying and weighing.

Difficulty would surely be encountered if any attempt were made to classify the known reagents in order of their value or even of their specific nature. Therefore, only a few of the more common ones and the metal ions for which they are most generally used will be mentioned.

One of the lesser known, yet one of the more specific reagents, is propylene diamine. A mixture of this compound with copper sulfate reacts quantitatively with mercury to form a complex of the formula $HgICu(Pn)_2$ containing 21.81% mercury.

An example of the double purpose reagent is $\alpha$-benzoin oxime. When this is dissolved in a suitable solvent and added to an ammoniacal solution, any copper present is quantitatively precipitated, while in acid solution only molybdenum is obtained in an insoluble form.

A bright red precipitate, which is easily identified, is obtained by the precipitation of cobalt with $\alpha$-nitroso-$\beta$-naphthol. While this reagent is especially valuable for the determination of cobalt, under suitable conditions it will also quantitatively form insoluble complexes with iron, palladium, and gold.

When using a chemical known to precipitate completely fifteen different metals and partially six others, it would seem impossible to obtain accurate results in the determination of only one of these metals. Yet in the case of ammonium nitrosophenylhydroxylamine (cupferron) such is possible by means of the careful control of conditions which render the reagent selective in its action. It is of special value for the determination of vanadium, titanium, iron, and zirconium.

One of the most versatile reagents in general use is 8-hydroxyquinoline which has, perhaps, received as much attention as any single compound. With it, as many as twenty-three metals are completely precipitated but in spite of this imposing array, it is extremely valuable as a selective precipitant. By control of the acidity of the solvent medium and by the addition of salts or organic acids which inhibit the formation of undesirable complexes, satisfactory procedures have been developed for the quantitative determination of a number of metals. Of especial interest is its use for aluminium, magnesium, and zinc. This is an example of a precipitating reagent in which the metal complex may be determined either gravimetrically by weighing, or bromometrically. For the latter method, the complex formed is brominated in hydrochloric acid by an excess of standard bromate-bromide solution, and the excess bromine determined iodometrically.

Many other similar organic reagents for gravimetric analyses, as well as further adaptations for other metals of those mentioned are known and are slowly coming into general use. Among them may be mentioned: quinaldinic acid for zinc; 8-hydroxyquinoline for bismuth; tannin and antipyrine for titanium; cyanamide for zinc; sodium 6-chloro-5-nitrotoluene-3-sulfonate for potassium; phenylarsonic acid for tin.

## *Colorimetric Reagents*

The second type of reagent is one in which a definite color is formed which is strictly proportional to the amount of compound present, consisting very often of only minute quantities. Comparison is made with solutions of known concentration or with artificial standards.

One of the best known of this type of reagent is "aluminon" or the ammonium salt of aurin tricarboxylic acid. In the presence of small amounts of aluminum, a red color is formed, while larger quantities produce a red precipitate.

Diphenylthiocarbazone, when dis-

solved in chloroform or carbon tetrachloride, forms a bright red solution with extremely small amounts of lead. It has also been recommended for similar tests with both mercury and zinc.

Silver in very low concentrations can be detected and determined with p-dimethylaminobenzalrhodanine. Sodium diethyl dithiocarbamate is one of the most sensitive tests for the determination of copper. Others which might be mentioned are p-nitrobenzeneazoresorcinol for magnesium and thioglycollic acid for iron.

# Preparation of Indicator Solutions

IN THE preparation of indicator solutions for determining hydrogen ion concentration, the solvents used and the indicator concentration vary according to the compound employed. Usually, there is a possibility of wide variation in the concentration without affecting the efficiency of the solution. The concentrations and solvents given in the tables below are in most cases those suggested in the numerous articles and books available on the subject. Their compilation here may serve to eliminate a search of the literature. Mimeographed copies of this list may be obtained without charge. The indicators included are those which are listed in the *Table of Hydrogen Ion Concentration Ranges (pH) and Color Changes of Eastman Organic Chemical Indicators.*

| *Indicator* | *Suggested Solution* |
|---|---|
| Alizarin Blue S | Alcohol |
| Aurin | .04 gm. in 40 cc. alcohol + 60 cc. water |
| Benzeneazodiphenylamine | 0.01 gm. in 1 cc. *N* HCl + 50 cc. alcohol + 49 cc. water |
| Benzopurpurin 4B | 0.1% in water |
| Congo Red | 0.1% in water |
| o-Cresolphthalein | 0.04% in alcohol |
| Curcumin | Alcohol |
| p-Dimethylaminoazobenzene | 0.1 gm. in 90 cc. alcohol + 10 cc. water |
| m-Dinitrobenzoyleneurea | 25 gm. in 115 cc. molar NaOH + 500 cc. boiling water, filtered and cooled. .292 gm. of the salt in 100 cc. water |
| 2,4-Dinitrophenol | Saturated water solution |
| 2,6-Dinitrophenol | 0.05% in water |
| Ethyl Orange | 0.05-0.2% in water or aqueous alcohol |
| Lacmoid | 0.2% in alcohol |
| Malachite Green | Water |
| Metanil Yellow | 0.01% in water |
| Methyl Orange | 0.01% in water |
| Methyl Red | 0.02 gm. in 60 cc. alcohol + 40 cc. water |
| Methyl Violet | 0.01-0.05% in water |
| α-Naphtholbenzein | 1% in dilute alkali |

(*Continued on page 4*)

| *Indicator* | *Suggested Solution* |
|---|---|
| Neutral Red | .01 gm. in 50 cc. alcohol + 50 cc. water |
| m-Nitrophenol | 0.3% in water |
| p-Nitrophenol | 0.1% in water |
| Orange II | 0.1% in water |
| Orange IV | 0.01% in water |
| Para-Methyl Red | Alcohol |
| Phenolphthalein | 0.05 gm. in 50 cc. alcohol + 50 cc. water |
| Phenoltetraiodophthalein Sodium Salt | Water |
| Picric Acid | Water |
| Propyl Red | Alcohol |
| Quinaldine Red | 1% in alcohol |
| Resazurin | Water |
| Sodium Alizarinsulfonate | Dilute solution in water |
| Sodium 2,4-Dihydroxyazobenzene-4-sulfonate | 0.01% in water |
| Sodium Indigodisulfonate | Water |
| Sodium Nitrobenzeneazosalicylate | 0.01% in water |
| p-Sulfo-o-methoxybenzeneazodimethyl-α-naphthylamine | 0.1% in 60% alcohol |
| Thymolphthalein | 0.04 gm. in 50 cc. alcohol + 50 cc. water |
| o-Toluneazo-o-toluidine | Water |
| 1,3,5-Trinitrobenzene | 0.1-0.5% in alcohol |
| 2,4,6-Trinitrotoluene | 0.1-0.5% in alcohol |

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Indicators of the sulfonphthalein type are supplied in the acid form. For use, the mono sodium salt is prepared and dissolved in water. The general procedure is to grind 0.1 gram of the dry indicator in a mortar with the required amount of alkali and to dilute the mixture to 250 cc. which gives a strength of 0.04%. In the following table, the figures given are the number of cubic centimeters of .01 *N* sodium hydroxide required to form the mono sodium salt.

| | |
|---|---|
| o-Cresolsulfonphthalein (Cresol Red) | 26.2 |
| m-Cresolsulfonphthalein (meta-Cresol Purple) | 26.2 |
| Dibromo-o-cresolsulfonphthalein (Bromcresol Purple) | 18.5 |
| Dibromothymolsulfonphthalein (Bromthymol Blue) | 16.0 |
| Dichlorophenolsulfonphthalein (Chlorphenol Red) | 23.6 |
| Phenolsulfonphthalein (Phenol Red) | 28.2 |
| Tetrabromo m-Cresolsulfonphthalein (Bromcresol Green) | 14.3 |
| Tetrabromophenolsulfonphthalein (Bromphenol Blue) | 14.9 |
| Tetraiodophenolsulfonphthalein | 11.7 |
| Thymolsulfonphthalein (Thymol Blue) | 21.5 |
| p-Xylenolsulfonphthalein (Xylenol Blue) | 24.4 |